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Diffusion coefficients and viscosities of organic aerosol components through equilibrium and non-equilibrium molecular dynamics simulations

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Organic aerosols have been typically considered to be liquid, with equilibration between gas and aerosol phase assumed to be reached within seconds. However, Virtanen et al. (Nature, 2010) suggested that particles in amorphous solid state may also occur in the atmosphere implying that mass transfer between the atmospheric particulate and gas phases may be much slower than initially thought. Experimentally, the direct measurement of the diffusion coefficients of different compounds inside atmospheric organic particles is challenging. Thus, an indirect approach is usually employed, involving viscosity measurements and then estimation of diffusion coefficients via the Stokes-Einstein equation, according to which the diffusion coefficient is inversely proportional to the medium viscosity. However, the corresponding diffusion estimates are highly uncertain, especially for highly viscous aerosols which is the most important case. Molecular simulation methods, such as molecular dynamics (MD), can be an alternative method to determine directly the diffusion rates and the viscosity of the constituents of atmospheric organic particles. MD also provides detailed information of the exact dynamics and motion of the molecules, thus offering a deeper understanding on the underlying mechanisms and interactions.

In the present work, we use equilibrium and non-equilibrium MD simulations to estimate the viscosity and diffusion coefficients of bulk systems of representative organic compounds with different chemical structures and physicochemical characteristics. Hydrophilic and hydrophobic compounds representative of primary and secondary oxidized organic products and of primary organic compounds emitted by various sources are considered. The viscosity and self-diffusion coefficients calculated by our simulations are in good agreement with available experimentally measured values. Our results confirm that the presence of carboxyl and hydroxyl groups in the molecule increases the viscosity. The number of carboxyl and hydroxyl groups, in particular, seems to have a good effect on diffusivity (the diffusivity decreases as the number of these functional groups increase), and to a lesser extent on the viscosity. We also discuss the role of the hydrogen bonds formed between these functional groups.